

Statistical Thermodynamics in Chemistry and Biology

15. Solutions and mixtures

Per-Olof Åstrand

D3-119 Realfagsbygget, Department of Chemistry,
Norwegian University of Science and Technology,
per-olof.aastrand@ntnu.no

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Lattice model for mixtures and solutions

This chapter:

- ▶ A lattice model for mixtures
- ▶ Ideal and regular solutions
- ▶ The mean-field approximation
- ▶ Basis for later chapters
- ▶ Foundation for treating polymers, colloids and biomolecules

Entropy of mixing

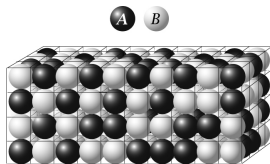
- ▶ Lattice model with N_A and N_B molecules of specie A and B , respectively.
- ▶ $N = N_A + N_B$ fill the lattice completely, see figure.
- ▶ A and B have the same size (see Ch. 32 for different sizes, Flory-Huggins).
- ▶ The multiplicity for the mixture, W_{AB} , is given as,

$$W_{AB} = \frac{N!}{N_A!N_B!}$$

- ▶ What is the multiplicity of the pure systems A and B ?

$$\Delta S_{\text{mix}} = S_{AB} - (S_A + S_B) = k_B \ln W_{AB} - (k_B \ln W_A + k_B \ln W_B) = k_B \ln W_{AB}$$

since $W_A = W_B = 1$.



Entropy of mixing

Part 2

- The entropy becomes (using Stirling's formula)

$$\begin{aligned}\Delta S_{\text{mix}} &= k_B \ln W_{AB} = k_B (N \ln N - N_A \ln N_A - N_B \ln N_B) \\ &= k_B (N_A \ln N + N_B \ln N - N_A \ln N_A - N_B \ln N_B)\end{aligned}$$

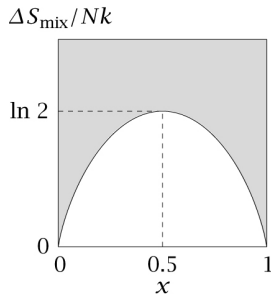
- Use **mole fractions**, $x_A = \frac{N_A}{N}$, $x_B = \frac{N_B}{N}$, $x_A + x_B = 1$.

$$\Delta S_{\text{mix}} = -k_B (N_A \ln x_A + N_B \ln x_B)$$

- Furthermore, use $x = x_A$ and $x_B = (1 - x)$,

$$\frac{\Delta S_{\text{mix}}}{Nk_B} = -x \ln x - (1 - x) \ln (1 - x)$$

- Note that x is fix in this model (no reactions), so it does not change to reach the maximum in the figure.



Ideal solutions

- ▶ For an **ideal solution**, the interactions between the particles are ignored (analogy to ideal gas),

$$\Delta F_{\text{mix}} = -T\Delta S_{\text{mix}}$$

- ▶ This model (ideal solutions) will not be used. Only included for the analogy to ideal gases.

Energy of mixing

- ▶ Same lattice model as in the previous chapter (only nearest-neighbour interactions),

$$U = m_{AA}w_{AA} + m_{BB}w_{BB} + m_{AB}w_{AB}$$

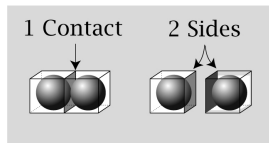
where m_{XY} is the number of bonds and w_{XY} is the interaction energy between species X and Y .

- ▶ Express m in terms of N_X . Each lattice site has z *sides*,

$$zN_A = 2m_{AA} + m_{AB} ; \quad zN_B = 2m_{BB} + m_{AB}$$

- ▶ Thus

$$m_{AA} = \frac{zN_A - m_{AB}}{2} ; \quad m_{BB} = \frac{zN_B - m_{AB}}{2}$$



Energy of mixing

Part 2

- The energy expression becomes,

$$\begin{aligned}
 U &= \frac{zN_A - m_{AB}}{2} w_{AA} + \frac{zN_B - m_{AB}}{2} w_{BB} + m_{AB} w_{AB} \\
 &= \frac{zw_{AA}}{2} N_A + \frac{zw_{BB}}{2} N_B + \left(w_{AB} - \frac{w_{AA} + w_{BB}}{2} \right) m_{AB}
 \end{aligned}$$

which needs to be simplified by a suitable approximation.

The mean-field (Bragg-Williams) approximation

- ▶ There are many different possibilities of m_{AB} that fulfills the macroscopic constraints ($F(T, V, N)$), which all should be included in a sophisticated model.
- ▶ In the **mean-field approximation**, the particles are mixed as randomly and as uniformly as possible.
- ▶ What is the probability that a B occupies a neighbouring site to an A ?
 - ▶ In the **Bragg-Williams** approximation, the B particles are distributed randomly.
 - ▶ The probability, p_B , that any site is occupied by B is,

$$p_B \approx \frac{N_B}{N} = x_B = 1 - x$$

- ▶ In reality, however, p_B , for a single site depends on the interaction energies, w_{XY} as well as which type of particle that occupies the neighbouring site.

The mean-field approximation

Part 2

- ▶ Since there are z neighbours to a particular A molecule, it has the average number of AB contacts,

$$zp_B = \frac{zN_B}{N}$$

- ▶ Since there is a total of N_A A molecules,

$$m_{AB} = \frac{zN_A N_B}{N} = zNx(1-x)$$

- ▶ The internal energy becomes,

$$\begin{aligned} U &= \frac{zW_{AA}}{2}N_A + \frac{zW_{BB}}{2}N_B + z \left(w_{AB} - \frac{w_{AA} + w_{BB}}{2} \right) \frac{N_A N_B}{N} \\ &= \frac{zW_{AA}}{2}N_A + \frac{zW_{BB}}{2}N_B + k_B T \chi_{AB} \frac{N_A N_B}{N} \end{aligned}$$

where χ_{AB} is termed the **exchange parameter**.

The mean-field approximation

Part 3

- ▶ The exchange parameter, χ_{AB} , is given as

$$\chi_{AB} = \frac{z}{k_B T} \left(w_{AB} - \frac{w_{AA} + w_{BB}}{2} \right)$$

- ▶ The Bragg-Williams model fail when there are big differences in the interaction energies, w , but it serves as a good first approximation.
- ▶ Note the *unfortunate* dependence of χ_{AB} on $k_B T$.

Free energy of mixing

- ▶ Since $F = U - TS$,

$$\frac{F(N_A, N_B)}{k_B T} = N_A \ln \frac{N_A}{N} + N_B \ln \frac{N_B}{N} + \frac{zW_{AA}}{2k_B T} N_A + \frac{zW_{BB}}{2k_B T} N_B + \chi_{AB} \frac{N_A N_B}{N}$$

- ▶ We are normally interested in the free energy difference, ΔF_{mix} between the mixed and the initial pure states,

$$\Delta F_{\text{mix}} = F(N_A, N_B) - F(N_A, 0) - F(0, N_B)$$

- ▶ The free energies of the pure states only consist of an internal energy term,

$$F(N_A, 0) = \frac{zW_{AA}N_A}{2} ; \quad F(0, N_B) = \frac{zW_{BB}N_B}{2}$$

- ▶ So the final result for ΔF_{mix} becomes,

$$\frac{\Delta F_{\text{mix}}}{Nk_B T} = x \ln x + (1 - x) \ln (1 - x) + \chi_{AB} x (1 - x)$$

which is termed the **regular solution model**.

The chemical potential of a mixture

- Free energy of **mixture** from previous slide,

$$\frac{F(N_A, N_B)}{k_B T} = N_A \ln \frac{N_A}{N} + N_B \ln \frac{N_B}{N} + \frac{zW_{AA}}{2k_B T} N_A + \frac{zW_{BB}}{2k_B T} N_B + \chi_{AB} \frac{N_A N_B}{N}$$

- Note that $F(N_A, N_B)$ and the definition of partial derivatives (differentiating with respect to N_A while keeping N_B fixed).
- Since $N = N_A + N_B$, we have to replace N with $N_A + N_B$ and then differentiate with respect to N_A .
- The chemical potential of the mixture for molecule A becomes

$$\frac{\mu_A}{k_B T} = \frac{1}{k_B T} \left(\frac{\partial F}{\partial N_A} \right)_{T, V, N_B} = \ln x_A + \frac{zW_{AA}}{2k_B T} + \chi_{AB} (1 - x_A)^2$$

(see derivation in eq. 15.17 in the book).

The chemical potential of a mixture

Activity coefficient

- ▶ From eq. 14.8, we have the chemical potential for a pure liquid, μ_A^o ,

$$\mu_A^o = \frac{ZW_{AA}}{2}$$

leading to

$$\mu_A = \mu_A^o + k_B T \ln x_A + k_B T \chi_{AB} (1 - x_A)^2$$

- ▶ In thermodynamics, the chemical potential is often expressed as

$$\mu_A = \mu_A^o + k_B T \ln \gamma x_A$$

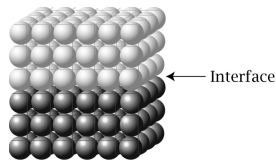
where γ (here!) is called the **activity coefficient**.

- ▶ Note the **inconsistency** in the dependency on x_A , and we try to avoid using the activity coefficient in this course.

Interfacial tension

- ▶ Regard the boundary between two condensed phases, the **interface**.
- ▶ The **interfacial tension**, γ_{AB} is the cost in free energy to increase the *interfacial area*.
- ▶ So if γ_{AB} is large the interfacial area will be small.
- ▶ Let us extend the lattice model for surface tension,

$$U = (N_A - n) \frac{zw_{AA}}{2} + n \frac{(z-1)w_{AA}}{2} + (N_B - n) \frac{zw_{BB}}{2} + n \frac{(z-1)w_{BB}}{2} + nw_{AB}$$



Interfacial tension

Part 2

- ▶ The entropy is 0 (i.e. no mixing) in this lattice model, leading to

$$\gamma_{AB} = \left(\frac{\partial F}{\partial A} \right)_{N_A, N_B, T} = \left(\frac{\partial U}{\partial A} \right) = \left(\frac{\partial U}{\partial n} \right) \frac{dn}{dA}$$

- ▶ Calculating the derivatives ($A = na$),

$$\left(\frac{\partial U}{\partial n} \right) = w_{AB} - \frac{w_{AA} + w_{BB}}{2} ; \quad \frac{dn}{dA} = \frac{1}{a}$$

the interfacial tension becomes,

$$\gamma_{AB} = \frac{1}{a} \left(w_{AB} - \frac{w_{AA} + w_{BB}}{2} \right) = \frac{k_B T}{za} \chi_{AB}$$

- ▶ Depending on the sign of χ_{AB} , γ_{AB} can have any sign. However, there is a competition between mixing and creating an interface, and mixing will occur if $\Delta F_{\text{mix}} < 0$.
- ▶ Is the interfacial tension, γ_{AB} , temperature-dependent? *No*

What have we left out?

- ▶ We should have evaluated the multiplicity W for each m_{AB} (number of AB interactions), and evaluated the partition function,

$$Q = \sum_{m_{AB}} W(N_A, N_B, m_{AB}) e^{-\beta E(N_A, N_B, m_{AB})}$$

where W is here also interpreted as a degeneracy factor

- ▶ Secondly, we have ignored the contributions from the molecular partition functions, q_A and q_B ,

$$\begin{aligned} \frac{F(N_A, N_B)}{k_B T} = & N_A \ln \frac{N_A}{N} + N_B \ln \frac{N_B}{N} + \frac{zW_{AA}}{2k_B T} N_A + \frac{zW_{BB}}{2k_B T} N_B + \chi_{AB} \frac{N_A N_B}{N} \\ & - N_A \ln q_A - N_B \ln q_B \end{aligned}$$

where q_X includes molecular vibrations, rotations, etc.

- ▶ However, regarding the free energy of the pure states,

$$\frac{F(N_A, 0)}{k_B T} = \frac{zW_{AA}N_A}{2k_B T} - N_A \ln q_A ; \quad \frac{F(0, N_B)}{k_B T} = \frac{zW_{BB}N_B}{2k_B T} - N_B \ln q_B$$

the molecular partition functions, q_X , do not contribute to the mixing free energy, ΔF_{mix} , if q_X do not depend on the interactions with the neighbours

Summary

- ▶ Lattice model for mixing and solutions
- ▶ Introduced the mean-field (Bragg-Williams) approximation.
- ▶ Calculated the free energy of mixing, ΔF_{mix} .
- ▶ Discussed interfacial tension.

E15.3(a-b) (Exam Aug. 2012:2)

Mixture and surface tension

a) Assume that we have a cluster (small drop) with e.g. methanol and chloroform. It is found that methanol has a higher concentration on the surface, whereas chloroform has a higher concentration in the centre of the cluster. Explain (not derive) this behaviour in terms of a lattice model (the curvature of the drop may be ignored) and a regular solution. What is a regular solution? Which are the driving forces? What would happen if all intermolecular interactions would be the same?

b) Use the same example as in a). Would methanol or chloroform have the highest surface tension (motivate the answer)? Explain what the surface tension is in terms of a lattice model.